

Lecture 7

Interaction forces I -

From interatomic and intermolecular forces to tip-sample interaction forces

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Further reading

- J. Israelachvili, "Intermolecular and surface forces".
- H. J. Butt, B. Cappella, M. Kappl, "Force measurements with the atomic force microscope: technique, interpretation and applications" *Surface Science Reports*, Vol. 59 (1-6), 1-152, 2005.
- K. L. Johnson "Contact Mechanics".

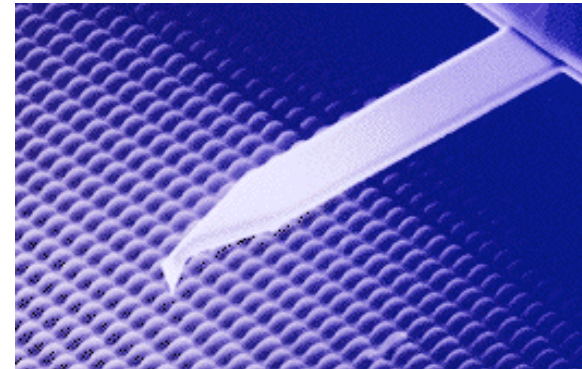
Microcantilever - the force sensor

OMCL-AC160TS series (type2)
 Rectangular cantilever with tetrahedral tip
 Tip location: Just on end of cantilever

Chip size of silicon cantilever
 One cantilever is extended from side edge of each chip

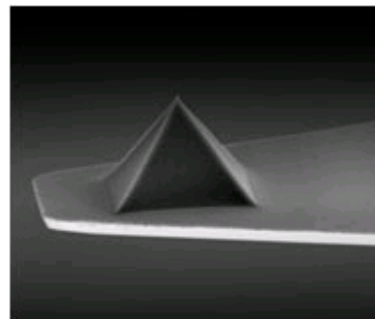
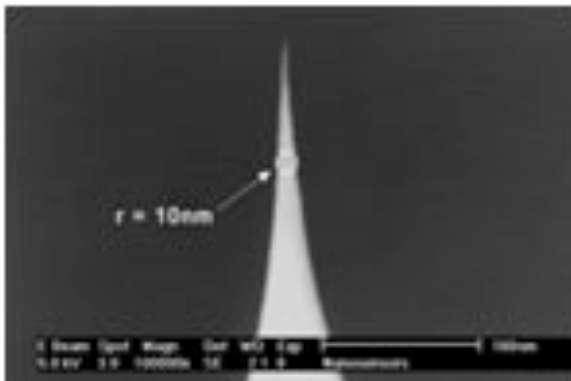
OMCL-AC160TS-
 unit: μm

unit: mm

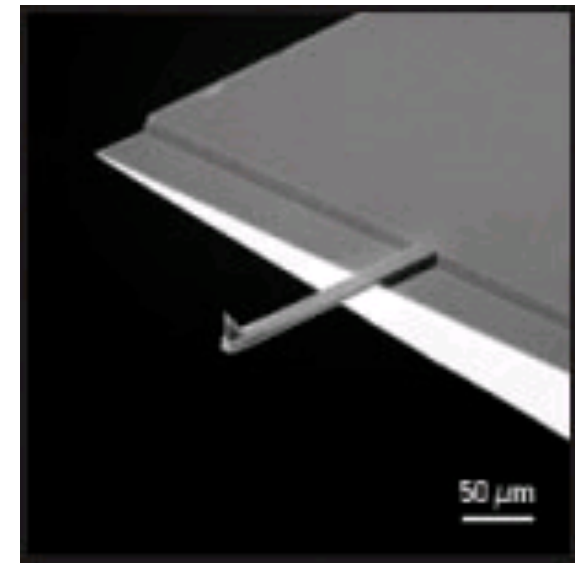


www.olympus.co.jp

www.nanosensors.com

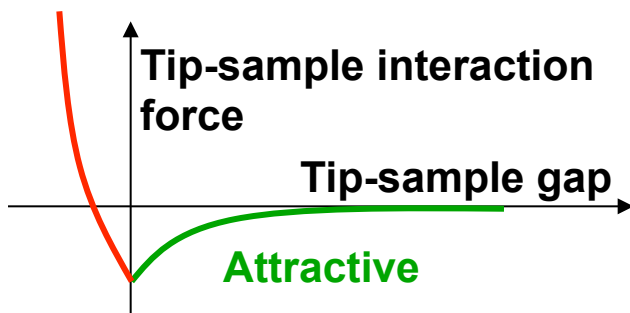
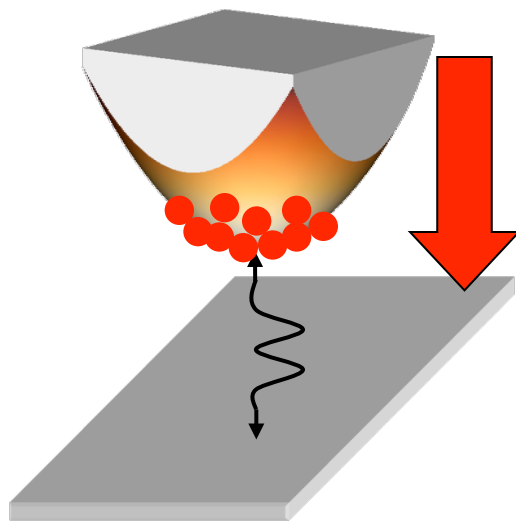
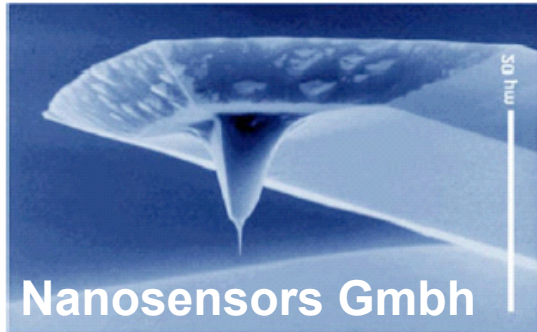


www.nanoworld.com



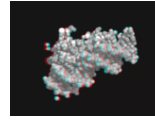
www.mikromasch.com

Tip-sample interaction forces in AFM



- Long-range electrostatic and magnetic forces (upto 100 nm)
- Short-range electrostatic forces
- Short-range polarization forces
- Dispersion forces (few nm) that are fundamentally quantum mechanical in nature
- Van der Waals and Casimir forces
- Capillary forces (few nm)
- Short-range chemical forces (fraction of nm)
- Pauli repulsion
- Contact forces
- Electrostatic double-layer forces
- Solvation forces
- Hydrophobic and hydrophilic forces
- Nonconservative forces (Dürig (2003))

Interatomic and intermolecular forces



A wide variety of forces act between atoms and molecules that can be loosely classified as follows (Israelachvili):

- **Electrostatic forces:** interactions between charged ions, permanent dipoles etc. fall into this category
- **Polarization forces:** these forces occur due to dipoles induced in some molecules in response to electric fields from nearby charges or permanent dipoles
- **Dispersion forces:** these are fundamentally electrodynamic in nature and occur between atoms and molecules even if they are charge neutral and without permanent dipoles
- **Covalent bond forces:** when two or more atoms come together to form a molecule and share electrons, the forces that tightly bind the atoms together are called covalent forces.
- **Pauli repulsion forces:** At very small interatomic distances the electron clouds of atoms overlap and there arises a strong repulsive force that determines how close two atoms or molecules can ultimately approach each other.

In each case the interaction force F can be written as a function of the separation r as follows $F(r) = -\frac{dU(r)}{dr}$ where $U(r)$ is the potential energy of the interaction.

Electrostatic interatomic and intermolecular forces

- Charge-charge (ion-ion) interactions:

$$U(r) = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r}, \text{ where } \epsilon_0 = 8.85418782 \times 10^{-12} \text{m}^{-3} \text{kg}^{-1} \text{s}^4 \text{A}^2$$

$$F(r) = -\frac{dU(r)}{dr} = \frac{Q_1 Q_2}{4\pi\epsilon\epsilon_0 r^2}$$

- Permanent dipole-charge interactions: A permanent dipole of an asymmetric molecule is the separation of charges in the molecule times the magnitude of the charge ($\mu = Ql$), its units are C-m or Debyes (D),
 $1\text{D} = 3.336 \times 10^{-30} \text{C-m}$

$$U(r) = -\frac{Q\mu \cos(\theta)}{4\pi\epsilon\epsilon_0 r^2}$$

- Permanent dipole-permanent dipole interactions:

$$U(r) = -\frac{u_1 u_2 [2\cos(\theta_1)\cos(\theta_2) - \sin(\theta_1)\sin(\theta_2)\cos(\phi)]}{4\pi\epsilon\epsilon_0 r^2}$$

Strength of interactions and angle averaging

The strength of an interaction is measured by comparing the value of the potential energy at equilibrium with $k_B T$ ($k_B = 1.3806503 \times 10^{-23} \text{ m}^2 \text{ kg s}^{-2} \text{ K}^{-1}$). For strong interactions $U \sim 100$'s of $k_B T$ ($k_B T = 4.1 \times 10^{-21} \text{ J}$ at 300K)

- Example 1 (2 electron charges $Q = 1.602 \times 10^{-19} \text{ C}$ at a distance of 0.276 nm (equilibrium separation of Na^+ and Cl^-) in vacuum

- Example 2: What is the distance at which the potential energy of interaction of two dipoles (1D) lined up with each other reach with $k_B T$?

- Angle averaged dipole-dipole interactions: At large distances $k_B T$ makes molecules fluctuate and rotate so that a weighted average needs to be taken yielding (This is also known as the Keesom interaction)

$$U_{\text{Keesom}}(r) = -\frac{u_1^2 u_2^2}{3(4\pi\epsilon\epsilon_0)^2 k_B T r^6}$$

Polarization forces

All atoms and molecules are polarizable. For a non-polar molecule, polarizability arises from the displacement of its negatively charged electron cloud relative to the positively charged nucleus

where a is the polarizability and E is the applied electric field. Since both dipole moment and electric fields are vectors it follows that technically a is a tensor. Usually a depends on the frequency of the electric field.



- **electronic polarizability:** a_0 has units $4\pi\epsilon_0 \times \text{molecule volume}$ so it is proportional to molecule size.
- **Polarizability of polar molecules:** For asymmetric molecules, in addition to electronic polarizability, there is an orientation polarizability so:

$$\alpha = \alpha_0 + \frac{u^2}{3k_B T} E \text{ (Debye - Langevin equation)}$$

- **Dipole-induced dipole interaction:** by taking the electric field generated by a fixed dipole and plugging into the above equation, and angle averaging the result one finds in which a_{01} and a_{02} are the electronic polarizabilities of the two molecules. If one replaces a_0 with the orientation polarizability $a = u^2/3k_B T$, we recover the Keesom force

$$U_{\text{Debye}}(r) = -\frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{(4\pi\epsilon_0 \epsilon)^2 r^6} = -\frac{C_D}{r^6}$$

Dispersion forces

Reversible Adhesion ↴

The London or Dispersion force is the most important contributor to van der Waals forces and acts between all molecules **irrespective of their polarization** for distances ranging from 2 Å to 10 nm. It is fundamentally quantum mechanical in nature and arises from induced dipole-induced dipole interactions. This is hard to calculate, it can be shown that for two similar atoms/molecules

$$U_{London}(r) = -\frac{4}{2} \frac{\alpha_0^2 h\nu}{(4\pi\epsilon_0 \epsilon)^2 r^6} = -\frac{C_L}{r^6}$$

and for dissimilar atoms/molecules

$$U_{London}(r) = -\frac{3}{2} \frac{\alpha_{01}\alpha_{02}}{(4\pi\epsilon_0 \epsilon)^2 r^6} \frac{(h\nu_1)(h\nu_2)}{h\nu_1 + h\nu_2} = -\frac{C_L}{r^6}$$

Anatomy of Gecko Foot
Autumn & Peattie Integr. Comp. Biol. (2002) ↴

- Extensions to frequency dependent polarizations by McLachlan (1963)
- As distances increase (>100nm), the time taken for fluctuating dipoles to reach other atom/molecule needs to be taken into account-retardation effects (power law dependence becomes 1/r⁷!)
- Casimir-Polder force is generalization to include finite conductivity

Historical aside: Lennard-Jones

Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character, Vol. 129, No. 811 (Nov. 3, 1930), 598-61

Perturbation Problems in Quantum Mechanics.

By J. E. LENNARD-JONES, Department of Theoretical Physics, The University, Bristol.

(Communicated by R. H. Fowler, F.R.S.—Received September 1, 1930)

1. *Introduction.*

One of the great achievements of the Schrödinger wave-mechanics elegance of its perturbation theory, which has brought many problems, formerly considered intractable, within the range of a highly-developed mathematical technique. It is not necessary at this stage to review the numerous applications which have been made of this perturbation theory or to dwell upon its many advantages. The important advance towards an understanding of chemical forces which it has made possible is in itself a considerable achievement.

There are, however, certain disadvantages in the perturbation theory in its present form, which limit the extent of its applications to complex problems of atomic and molecular structure. If the interaction of atoms, for instance, is to be calculated, as is most desirable, improved methods will have to be found.

One such improvement is considered in this paper. In its present form, it is easy to calculate the first approximation of the energy of a system, subject to small perturbations, but difficult to proceed further. This is a considerable disadvantage in those problems where the first approximation vanishes as in calculating the Stark effect or the van der Waals attraction of two atoms at large distances apart. Moreover, the theory expresses the perturbed eigenfunction in terms of all the unperturbed eigenfunctions of

5. *The Interaction of Two Hydrogen Atoms at Large Distances.*

The results of the preceding paragraphs may be applied to a number of problems, but it is instructive to apply the methods of this paper to a problem which has already been considered by the usual methods. A problem recently considered is that of the interaction of two hydrogen atoms at a large distance.* Eisenschitz and London carry out the Heitler and London† calculations to a second approximation, but find that these can only be carried out numerically when the distance between the atoms is large. For large distances the usual ‘austausch’ effect can be neglected and the unperturbed eigenfunction written simply as a product of the separate hydrogen eigenfunctions, viz.,

$$u_1 = \psi_1(1) \phi_1(2).$$



The first term of the summation $\sum_{n'n''}$ is equal to 0.051, and all the rest (including (i) the discontinuous range of n' with that of n'' , (ii) the continuous range of one with the discontinuous range of the other, (iii) the continuous range of both) only yields — 0.011.

We thus get

$$\eta = - \frac{e^2}{a_0 (R/a_0)^6} 12 (0.540) = - \frac{175}{(R/a_0)^6} \text{ volts,}$$

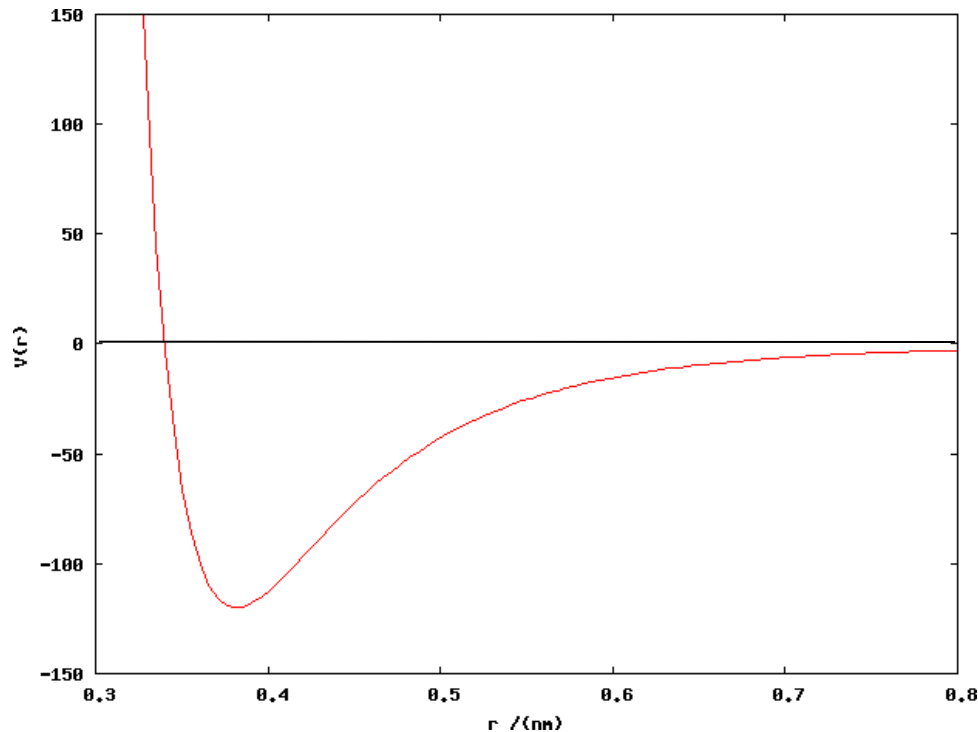
as do Eisenschitz and London, but the ease of calculation is to be compared with that involved in equation (57). The latter involve series of slow convergence, which can only be evaluated with great labour. The results are summarised in the following table :—

The Lennard-Jones potential

- Simple ad hoc model that tries to couple dispersion and Pauli-repulsion.

$$U(r) = 4U^* \left[\left(\frac{r^*}{r} \right)^{12} - \left(\frac{r^*}{r} \right)^6 \right]$$

- U^* is depth of potential, r^* is value at which $U(r^*)=0$
- While attractive part follows general dispersion relation but the repulsive part is adhoc



Van der Waals Forces

The van der Waals forces is the sum of three different forces each of whose potential varies as $1/r^6$, where r is the separation

- **Orientation or Keesom Force.** The Keesom force is the averaged dipole-dipole interaction between two atoms or molecules.
- **Debye Force** is the angle averaged dipole-induced dipole interaction between two atoms or molecules
- **The London or Dispersion force** is the most important contributor to van der Waals forces and acts between all molecules irrespective of their polarization.

$$\begin{aligned}
 U_{VdW}(r) &= U_{Keesom}(r) + U_{Debye}(r) + U_{London}(r) \\
 &= -\frac{u_1^2 u_2^2}{3(4\pi\epsilon\epsilon_0)^2 k_B T r^6} - \frac{u_1^2 \alpha_{02} + u_2^2 \alpha_{01}}{(4\pi\epsilon_0 \epsilon)^2 r^6} - \frac{3}{2} \frac{\alpha_{01} \alpha_{02}}{(4\pi\epsilon_0 \epsilon)^2 r^6} \frac{(h\nu_1)(h\nu_2)}{h\nu_1 + h\nu_2} = -\frac{C}{r^6}
 \end{aligned}$$

Implications for AFM

- In AFM the tip usually has native oxide on the tip within which small trapped charges or permanent dipoles can exist. As debris accumulates more permanent dipoles and charges accumulate on tip
- Dispersion potential scales as r^{-6} while electrostatics scales as r^{-1} or r^{-2}
- In reality attractive forces are due to combination of VdW and short range electrostatics

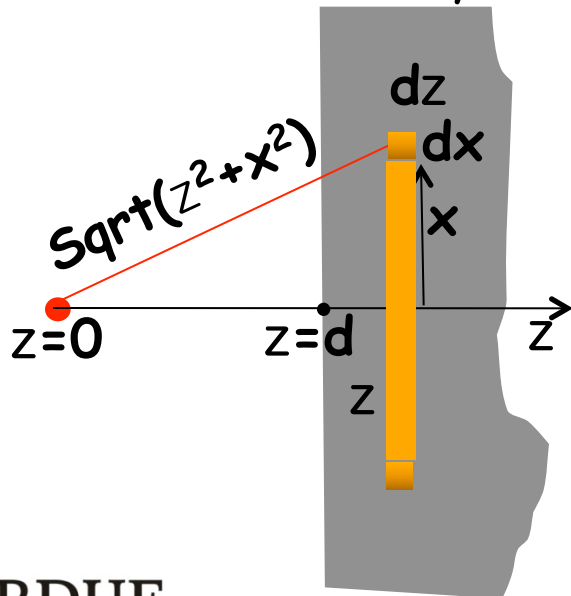
From interatomic to tip-sample interactions-simple theory

First consider the net interaction between an isolated atom/molecule and a flat surface.

Assume that the pair potential between the atom/molecule and an atom on the surface is given by $U(r)=-C/r^n$.

Assume additivity, that is the net interaction force will be the sum of its interactions with all molecules in the body.

No. of atoms/molecules in the infinitesimal ring are $2\pi r x dx dz$ where ρ is the number density of molecules/atoms in the surface



$$U(d) = -2\pi C\rho \int_{\zeta=d}^{\zeta=\infty} d\zeta \left(\int_{x=0}^{x=\infty} \frac{dx}{\left(\sqrt{\zeta^2 + x^2}\right)^n} \right)$$

$$= \frac{-2\pi C\rho}{(n-2)(n-3)d^{n-3}}, \quad \text{for } n > 3$$

$$U_{vdW} = \frac{-\pi C\rho}{6d^3}$$

From interatomic to tip-sample interactions-simple theory

Next integrate atom-plane interaction over the volume of all atoms in the AFM tip. Number of atoms/molecules contained within the slice shown below is $\rho x^2 dz = \rho (2R_{tip} - z)z dz$. Since all these are at the same equal distance $d+z$ from the plane, the net interaction energy can be derived by using the result on the previous slide.

$$U(d) = \frac{-2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=2R_{tip}} \frac{(2R_{tip} - \zeta)\zeta d\zeta}{(d + \zeta)^{n-3}}$$

If $d \ll R_{tip}$,

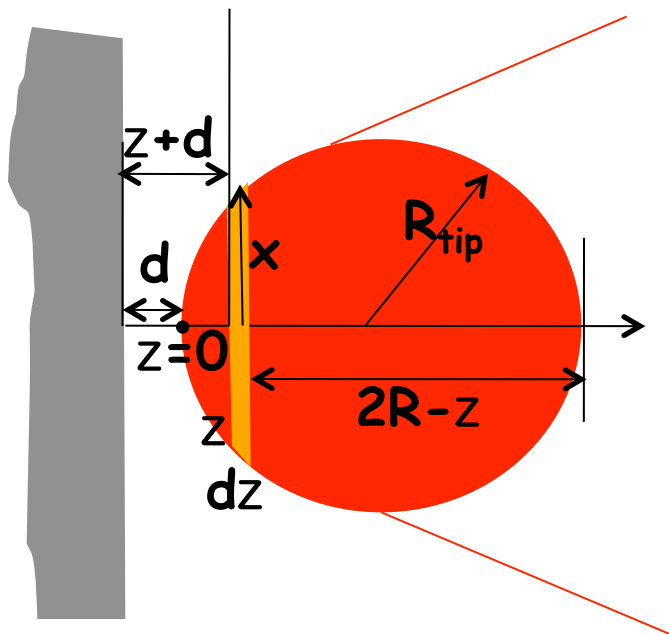
$$U(d) \sim \frac{-2\pi^2 C \rho^2}{(n-2)(n-3)} \int_{\zeta=0}^{\zeta=\infty} \frac{R_{tip} \zeta d\zeta}{(d + \zeta)^{n-3}}$$

$$= -\frac{4\pi^2 C \rho^2 R_{tip}}{(n-2)(n-3)(n-4)(n-5)d^{n-5}}$$

For $d \ll R_{tip}$, $n = 6$

$$U_{vdW}(d) \sim -\frac{\pi^2 C \rho^2 R_{tip}}{6d} = -\frac{H R_{tip}}{6d}$$

H : Hamaker's constant



From interatomic to tip-sample interactions-some caveats

- If tip and sample are made of different materials replace r^2 by $r_1 r_2$ etc.
- Tip is assumed to be homogeneous, sample also! Both made of "simple" atoms/molecules
- Assumes atom-atom interactions are independent of presence of other surrounding atoms
- Perfectly smooth interacting surfaces
- Tip-surface interactions obey very different power laws compared to atom-atom laws

Historical aside: Hamaker

Physica IV, no 10

23 November 1937

THE LONDON—VAN DER WAALS ATTRACTION BETWEEN SPHERICAL PARTICLES

by H. C. HAMAKER

Natuurkundig Laboratorium der N.V. Philips' Gloeilampenfabrieken Eindhoven-Holland

Summary

Frequently we experience the existence of adhesive forces between small particles. It seems natural to ascribe this adhesion for a large part to London-v. d. Waals forces. To obtain general information concerning their order of magnitude the London-v. d. Waals interaction between two spherical particles is computed as a function of the diameters and the distance separating them. A table is calculated which enables numerical application of the formulae derived. Besides approximations are added, which may be used when the distance between the particles is small. In a separate section it is investigated how the results must be modified, when both particles are immersed in a liquid. Here we are led to the important conclusion that even in that case London-v. d. Waals forces generally cause an attraction.

§ 1. *Introduction.* Frequently we experience the existence of adhesive forces between small particles of any substance or between a particle and a surface. Of this the general occurrence of flocculation in colloidal systems is one of the most striking examples.

It seems natural, to date, to attribute this adhesion mainly to London-v. d. Waals forces and it may be of interest to possess formulae from which the magnitude and range of these forces can be estimated. It is the purpose of this paper to provide some data which may be used for such computations. To simplify the calculations we will consider spherical particles only; in practical problems the particles will mostly be of irregular shape; in such cases the formulae derived below must be applied with caution, a question that will be discussed more in detail in a subsequent paper¹⁾.

The energy of interaction between two particles containing q atoms per cm^3 is given by:

$$E = - \int_{V_1} dv_1 \int_{V_2} dv_2 \frac{q^2 \lambda}{r^6} \quad (1)$$

— 1058 —

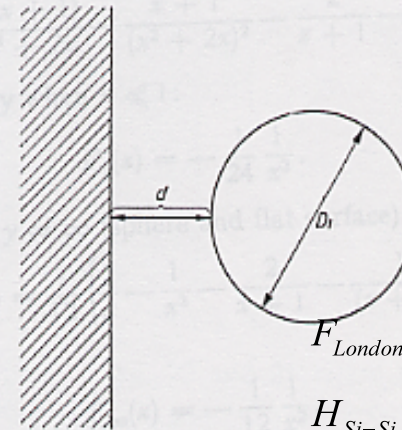


Fig. 3.

$$F_{London}(r) = - \frac{HR}{6r^2}$$

$$H_{Si-Si} = 6.76 \text{ eV}$$

$$1 \text{ eV} = 1.60217646 \times 10^{-19} \text{ J}$$

Likewise $y = \infty$ represents the case of a sphere and an infinite mass bounded by a flat surface (fig. 3). We have:

$$E_{\infty}(x) = \frac{1}{12} \left\{ \frac{1}{x} + \frac{1}{x+1} + 2 \ln \frac{x}{x+1} \right\} \quad (15)$$

and

$$E_{\infty}(x) = \frac{1}{12x} \quad \text{when } x \ll 1. \quad (15)$$

Next lecture

- More on contact mechanics theories